PERFORMANCE OF LI-ION RECHARGEABLE BATTERIES ASSEMBLED WITH ELECTRODES PREPARED FROM DEVELOPED SRI LANKAN VEIN GRAPHITE AND NANOSTRUCTURED $\mathrm{Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}Na_x)O_2}$

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ABSTRACT

Rechargeable batteries, such as Lithium Ion Batteries (LIBs,) offer viable solutions for storing electrical energy harnessed through solar cells and other renewable energy sources such as hydro, wind and biomass. Investigation of low cost and performance enhanced electrode materials for LIBs is an important task for the advancement of the next generation of LIBs. In this context, Sri Lankan natural vein graphite has been identified as a promising anode material for the LIBs. Moreover, the Na doped $\mathrm{Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2}$ cathode material shows further enhanced electrochemical performance. However, the performance of full LIB cell comprising a vein graphite anode has not yet been reported. Hence this abstract presents the outcome of our study conducted on a full LIB cells assembled with electrodes fabricated from developed Sri Lankan vein graphite and locally synthesized nanostructured $\mathrm{Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}Na_x)O_2}$

For the anode electrode preparation, vein graphite (99.99 % carbon) purified through acid leaching was further modified by mild chemical oxidation. For the cathode, phase pure nano-structured $\mathrm{Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}Na_x)O_2}$ was locally synthesized by employing the glycine nitrate combustion technique. The electrodes were fabricated by tape casting the developed electrode materials onto respective current collectors by employing the doctor blade method. Finally, CR2032 type LIB coin cells were assembled with these electrodes together with the non-aqueous liquid electrolyte of $\mathrm{LiPF_6}$.

The initial discharge capacity of the cell assembled using the developed graphite anode and $\mathrm{Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2}$ cathode was 98 mA h g^{-1} at C/5 rate between 3.0 and 4.2 V, at room temperature. More interestingly, the cell assembled with the Na doped $\mathrm{Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}Na_x)O_2}$; $x= 0.04$ cathode with the same graphite anode showed a higher discharged capacity of 135 mA h g^{-1} under the same operational condition. Furthermore, this full cell showed a higher capacity retention over cycling. Altogether, it clearly shows the very promising cell performance of full LIB cell comprised of electrode fabricated from developed Sri Lankan vein graphite and locally synthesized nano-structured $\mathrm{Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}Na_x)O_2}$.

Keywords: vein graphite, $\mathrm{Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}Na_x)O_2}$, lithium-ion batteries, cell performance.

1. INTRODUCTION

Invention of new techniques to store more energy is a crucial area of research to address the increasing challenge of energy needs for the present technology era. Rechargeable Lithium Ion Battery (LIB) is a very promising rechargeable energy storage device. Current LIBs are based on the expensive electrode materials such as synthetic graphite as the anode material and lithium cobalt oxides as the cathode material. However, the high unit cost and unsolved materials-related problems are keeping the LIBs from reaching the common masses as a cheaper and reliable portable power source [1]. Modified vein graphite in Sri Lanka has been identified as a cost effective alternative to the synthetic graphite [2]. However, effect of vein graphite anode on the performance of LIB has not yet been identified. Therefore, present study aims to investigate the electrochemical performance of lithium ion battery employing anode fabricated from purified vein graphite in Sri Lanka and performance enhanced $Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}Na_x)O_2$ cathode material synthesized by Glycine Nitrate Combustion (GNC) method.

2. METHODOLOGY

Vein graphite was purified up to 99.99 % carbon by employing acid leaching technique [3] followed by, mild chemical oxidation using $(NH_4)_2S_2O_8$ [4]. Raw graphite, purified graphite by acid leaching and mild oxidized vein graphite after purification are denoted here as RG, PG and SPG, respectively. $Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}Na_x)O_2$ cathode material was synthesized from glycine nitrate combustion process followed by calcined at 900 ^{0}C for two hours [5]. X-ray diffractometry (XRD) and Scanning Electron Microscopy (SEM) were used for phase analysis and particle characterization respectively. FTIR dense pellets of electrode materials were used for electrical characterization by D.C. four probe technique.

Electrodes were prepared by manual tape casting of electrode slurry onto a respective current collector by doctor blade method. The anode slurry was prepared by mixing 9:1 weight ratio of active material and PVdF in acetone as binder. The cathode slurry was prepared by mixing 8.5: 0.5: 1 weight ratio of active material, carbon black and PVdF in acetone. Coin cell type lithium ion cells were assembled using fabricated electrode in an argon-filled glove-box with a porous polypropylene separator in an non-aqueous electrolyte, 1M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC)/ dimethyl carbonate (DMC) (1:1:1 ratio in weight). The charge discharge studies were carried out at C/5 rate with a cut-off voltage of 3 - 4.2 V at room temperature using Scribner 580 Battery Testing System controlled by BCycle 2.0 programme.

3. RESULTS AND DISCUSSION

Fig.1 illustrates the XRD spectra of raw graphite, purified graphite by acid leaching and mild oxidized vein graphite after purification. The diffraction patterns consist of characteristic diffraction peaks of highly crystalline graphite. It indicates that the purification and mild oxidation processes did not affect the crystal structure. XRD peaks corresponding to the sulphate and carbonate impurities in RG are marked in (•) in Fig.1. This infers that the acid leaching purification process is an effective method both for the removal of sulphide and carbonate impurities at low temperature [3].

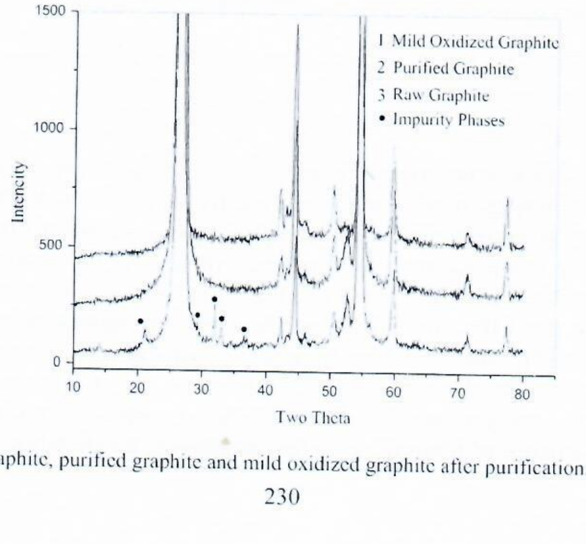


Fig.1.XRD pattern of raw graphite, purified graphite and mild oxidized graphite after purification.

Fig.2 shows the FTIR spectra of purified graphite and surface modified graphite. Vibrational bands correspond to $\nu_{C=O}$ stretching at 1720-1680 cm^{-1}, $\nu_{O\text{-}H}$ stretching at 1360 cm^{-1} and $\nu_{C\text{-}O}$ stretching at 1260-1000 cm^{-1} are predominant on the FTIR spectrum of the SPG surface compare to that of PG . Those bands reflect the modification of graphite surface structure by the formation of oxidized species on the edge plane of the graphite. D.C electrical conductivity measurements indicate that the PG and SPG processes sufficient electrical conductivity between 0.7 and 1 S/cm at room temperature sufficient for the anode application.

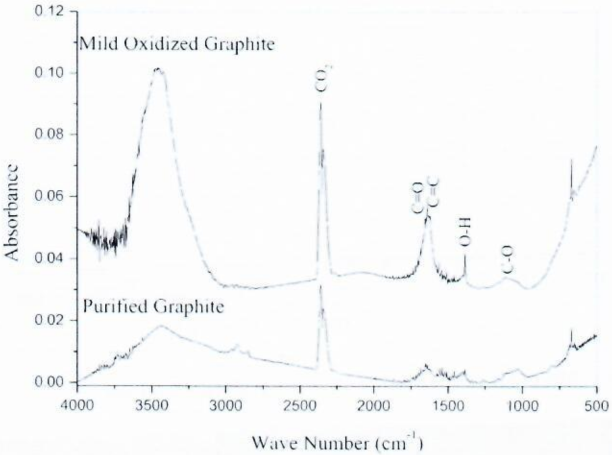


Fig.2 FTIR spectrum of purified graphite and mild oxidized graphite .

Fig.3 shows the XRD spectra of the synthesized $Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}\ Na_x)O_2$, $x = 0.00$, 0.04 materials in this study. In this figure, existence of the appropriate R3m phase of α-$NaFeO_2$ layered structure of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ phase can be seen in all these powder samples [6]. Fig.4 shows the SEM images obtained on $(Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}\ Na_x)O_2$, $x = 0,00$ and 0.04 materials. The SEM images indicate that all the powder samples comprise of well crystallized particles. Rather quasi-spherical particles with two different particle sizes can be clearly identified in these materials. The bigger secondary particles are seen as soft agglomerates of the size of few microns formed by agglomerating nano-scale primary particles. D.C electrical conductivity measurements indicate that the synthesized $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ processes sufficient electrical conductivity of 8.0 x 10^{-7} S/cm at room temperature.

Fig.4 (a) shows the charge-discharge curves of the first ten cycles of full cell assembled with mild oxidized vein graphite with $(NH_4)_2S_2O_8$ as anode and $Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}Na_x)O_2$; $x=$ 0.04 as cathode with a cutoff voltage range of 3 - 4.2 V, at C/5 rate (1 C = 140 $mAhg^{-1}$,based on the mass of $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$) The corresponding electrochemical data from first ten cycle charge-discharge curves presented in Fig.4 (b). This cell exhibits a charge and discharge capacity of about 168.0 and 135 mA h g^{-1}, respectively with coulombic efficiency of 80.2 %. It is the highest discharge capacity reported among the assembled vein graphite and synthesized cathode material in this study.

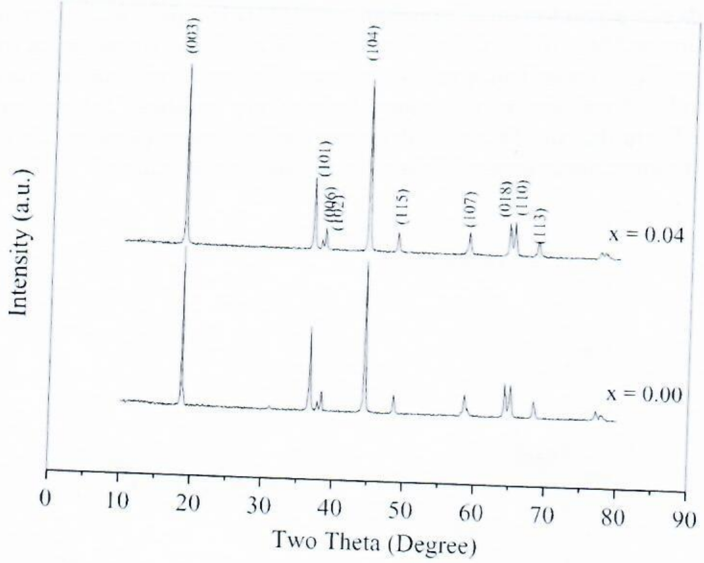
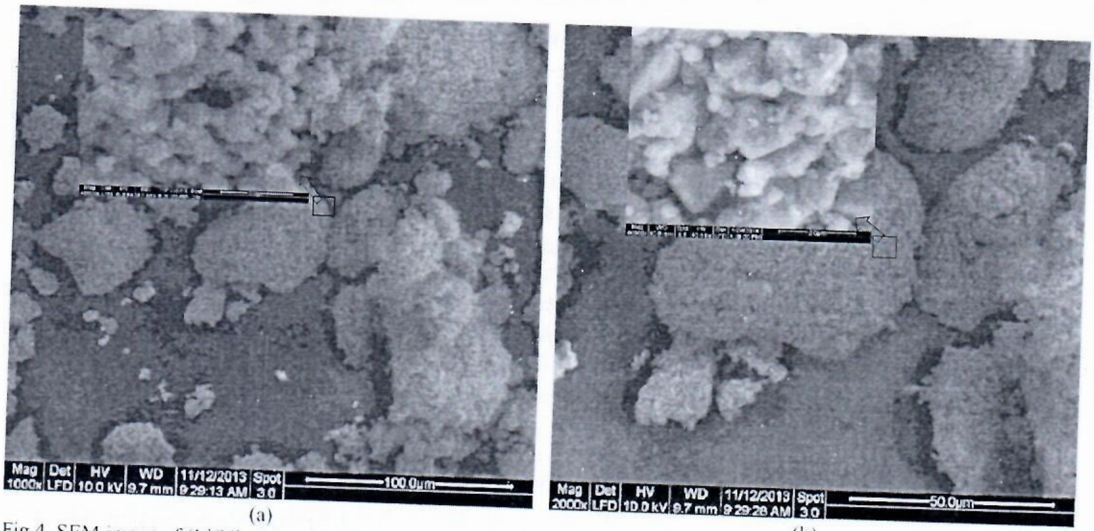
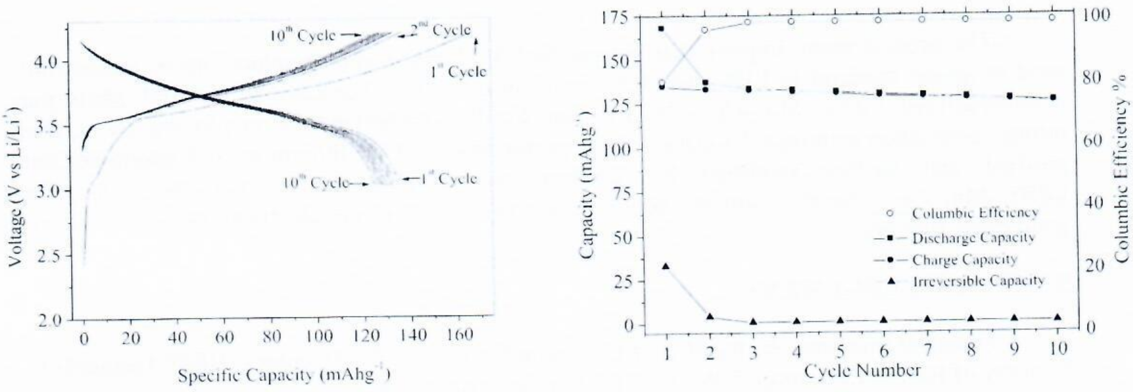


Fig.3. XRD pattern and (b) SEM image of $(Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}Na_x)O_2$, x = 0.00 and 0.04 .



(a)
(b)

Fig.4. SEM image of $(Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}Na_x)O_2$, x = (a) 0.00 and ((b) 0.04.



(a) (b)

Fig.4. (a) The charge-discharge curves of the first ten cycles of full cell assembled with mild oxidized vein graphite (purified) with $(NH_4)_2S_2O_8$ as anode and $Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}Na_x)O_2$; x= 0.04 as cathode with a cutoff voltage range of 3 - 4.2 V, at C/5 rate (1 C = 140 mAhg^{-1},based on the mass of $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$) and (b) The corresponding electrochemical data calculated from the first ten cycles.

Fig.5 shows variation on discharge capacity vs cycle number of full cells assembled with developed vein graphite/ $Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}Na_x)O_2$ (x = 0.00, 0.04) between 3 and 4.3 V at the C/5 rate based on weight of cathode. Among the assembled LIB cell, vein graphite / $Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}Na_x)O_2$ (x = 0.00) full cell delivered the lowest initial discharge capacity of 93.6 mAhg^{-1} at the C/5 rate. More importantly, vein graphite (purified)/ $Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}Na_x)O_2$ (x = 0.04) full cell shows the highest discharge capacity and capacity retention over the cycle.

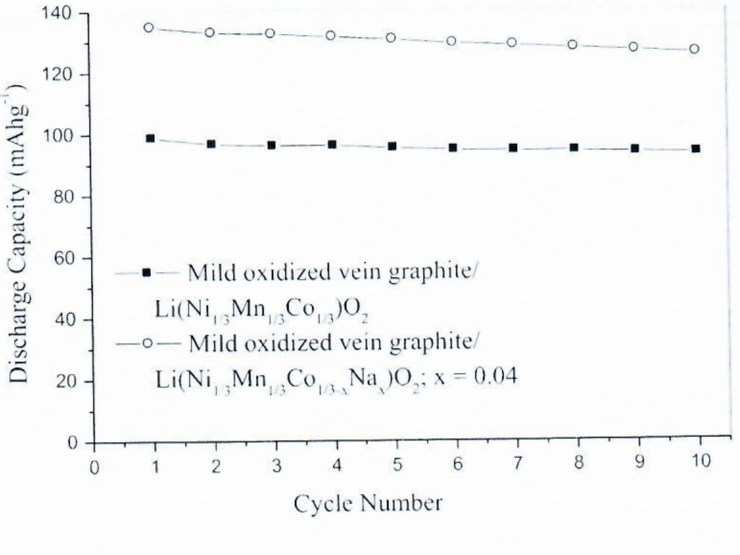


Fig.5. Discharge capacities vs. cycle number full cell assembled with developed vein graphite as anode and $Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}Na_x)O_2$; x = 0.04 as cathode with a cutoff voltage range of 3 - 4.2 V, at C/5 rate (1C = 140mA h g^{-1},based on the mass of $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$).

4. CONCLUSION

The present study implies that the purified Sri Lankan vein graphite can be successfully used as anode material in LIB after mild chemical oxidation. For cathode material, phase pure nano-structured $Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}Na_x)O_2$ was locally synthesized by employing the glycine nitrate combustion technique.Electrochemical performances of the lithium ion cell assembled with purified and surface modified Sri Lankan vein graphite anode and the synthesized $Li(Ni_{1/3}Mn_{1/3}Co_{1/3-x}Na_x)O_2$ cathode demonstrates promising electrochemical performance with good cycle stability.

5. ACKNOWLEDGEMENT

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6. REFERENCES

[1] Scrosati B., Garche J., *J. Power Sources* 195 (2010) 2419-30.
[2] Balasooriya N.W.B., Touzain Ph., Bandaranayake P.W.S.K., *J. Physics and chemistry of Solid* 67 (2006) 1213-1217.
[3] Amaraweera G., Balasooriya N., Wijayasinghe A., Attanayake N., Dissanayake, L. *7th International Conference on Materials for advanced Technology, Suntec, Singapore* (2013) A-2784.
[4] Amaraweera, T.H.N.G., Balasooriya, N.W.B., Wijayasinghe, H.W.M.A.C., Attanayake A.N.B., Dissanayake, M.A.K.L., *30th Technical Sessions of Geological Society of Sri Lanka, Sri Lanka* (2013) 101-104.
[5] Amaraweera, T.H.N.G., Senarathna D., Wijayasinghe A., *Ceylon Journal of Science* 45(3) (2016) 21-27.
[6] Samarasingha P., Tran-Nguyen D.-H., Behm M., and Wijayasinghe A., *Electrochimica Acta* 53 (2008) 7995- 8000.